Optimization of Experimental Conditions for Improvement of Bio-Methane Production by De-Polymerization of Agro Waste: A Waste to Energy Approach

SHORT SYNOPSIS

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by

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MANAV RACHNA UNIVERSITY
(FORMERLY MANAV RACHNA COLLEGE OF ENGINEERING
NAAC ACCREDITED 'A' GRADE INSTITUTION)
Declared as State Private University under section 2f of the UGC act, 1956

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DECLARATION BY THE SCHOLAR

I hereby declare that the short synopsis **"Optimization of experimental conditions for improvement of bio-methane production by de-polymerization of agro waste: a waste to energy approach"** being submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in department of Chemistry under Faculty of Applied Science of Manav Rachna University, Faridabad during the academic year2020-21.

It is a bona-fide record of original work carried out under the supervision of **Dr. Megha Bansal (Supervisor)**and **Dr. Vinayak Vandan Pathak (Co-Supervisor)** has not been submitted in full or part to any other university or institute for degree or diploma. Further, it is certified that short synopsis is within the plagiarism limit and copy of the same is attached as per University norms.

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ABSTRACT

Energy is the fundamental factor for any developing or developed countries, which is accomplished by various renewable and non renewable energy resources. It has become increasingly obvious that continued reliance on fossil fuel energy resources is unsustainable, owing to both depleting world reserves and the green house gas emissions associated with their use. Therefore, there are vigorous research initiatives aimed at developing alternative renewable and potentially carbon neutral solid, liquid and gaseous biofuels as alternative energy resources. Lignocellulosic biomass is a rich organic material that can be used for sustainable production of bioenergy. However, the utilization of lignocelluloses biomass for biogas production via anaerobic digestion has not been widely adopted because the complicated structure of the plant cell wall makes it resistant to microbial attack. Pretreatment of renitent lignocellulosic biomass is essential to achieve high biogas yield in the AD process. A number of different pretreatment techniques involving physical, chemical, and biological approaches have been investigated over the past few decades, but there is no report about optimization of experimental conditions for enhancing biogas production from lignocellulosic biomass. In this research proposal, chemical pretreatments will be performed for de-polymerization of lignocellulosic biomass. It is expected from the present study that the production of bioenergy will be enhanced by chemically modified methods of pre-treatment and de-polymerization

Key Words: Bio-energy; Biomass; Anaerobic digestion; Pretreatment; De-polymerization

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1. Introduction

India is a land of agriculture thus, a huge producer of agricultural waste as well. In spite of various waste management programs, the annual production of agricultural waste surpasses all management schemes and we either end up as landfills or burning of waste. On the other side this waste is having lot of potential for energy generation and formation of other bio based products. This crop residue can be used in many fields like textile manufacturing processes, electricity generation, bioenergy production, animal fodder, fertilizer and manures etc.(Saroj Devi et al.,2017).From the various options for crop residue management. Bio-energy production is the best one due to limited stock and harsh effect of fossil fuel energy resources on environment. As the fossil fuel resources are non-renewable and have harsh effect on environment, so it is a need of hours to find out renewable, economic and clean alternative energy resource that can fulfil the demand of energy of world population. This criterion enhances the interest of scholars in research and development of renewable clean alternative of energy that can minimise pollution. In this direction many attempts has been done that results in first, second and third generation bio fuels.

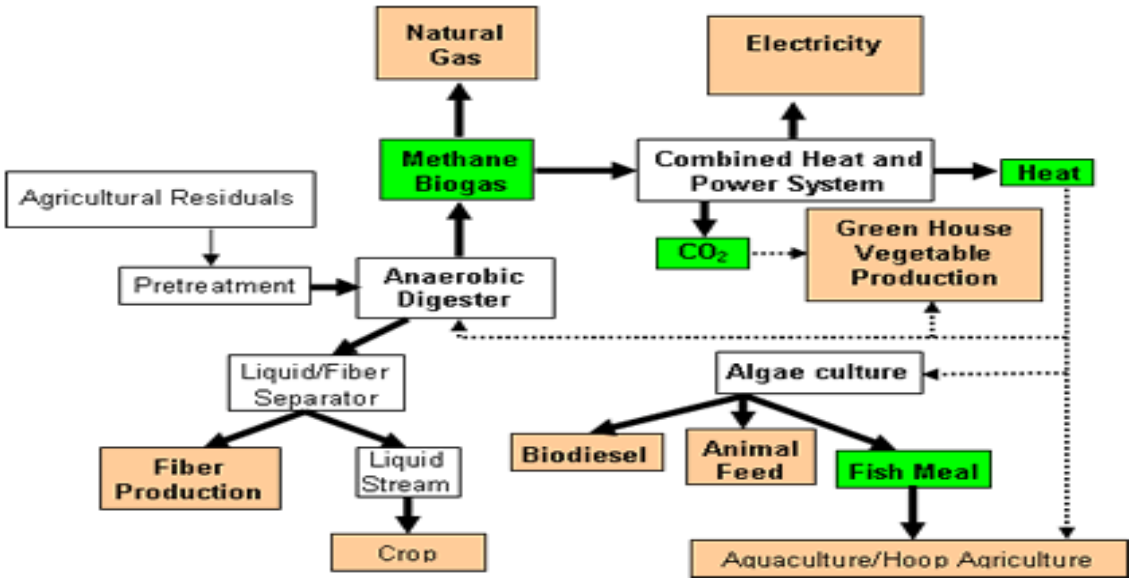

Figure: 1 Agricultural residue as a good source of bioenergy production (Source: Kothari et al., 2017)

If the fuels are derived from starch, sugar, animal fats and vegetable oils it is called as first generation biofuels. But the first generation biomass have a limit for conversion to biofuels as these have a threshold value above which it disturbs food supplies and biodiversity. Due to large limitations of first generation biofuels, second generation biofuels techniques have been developed. Second generation biofuels are obtained from agro-food waste like crop residue or lignocellulosic agriculture waste like leaves straws, stems and husks. They are good source of cellulose, hemicelluloses and lignin. Second generation biofuels are beneficial in such a manner

Agricultural residue	Cellulose	Hemicellulose	Lignin
Hardwood stem	40–50	24–40	18–25
Softwood stem	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Wheat straw	33–40	20–25	15–20
Rice straw	40	18	5.5
Leaves	15–20	80–85	0
Sorted refuse	60	20	20
Cotton seed hairs	80–90	5–20	0
Coastal Bermuda grass	25	35.7	6.4
Switch grass	30–50	10–40	5–20
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Swine waste	6.0	28	
Primary wastewater solids	8–15	NA	24–29
Paper	85–99	0	0–15
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–20	5–10

Table1.Cellulose, Hemicelluloses and lignin content in various Agricultural residuew (Source: Prasad et al., 2007)

that they capture energy from waste using the valuable fields for food/crop production. Thus, production of bio-energy from anaerobic digestion has a good way for conversion of biomass to bioenergy (Khor et al., 2015; Menardo et al., 2012; Sambusiti et al., 2013). So, this way of conversion of non-edible agro-waste biomass to bioenergy is preferred over the conversion of edible food or oils that makes exasperate pressures on food supplies (Sims et al., 2010).

In India, abundant of crops are produced among which production of wheat and rice is largest, hence their agro-waste are also most abundantly available. As wheat straw is a lignocellulosic biomass, it is a complex composition of cellulose, hemicelluloses and lignin (Prasad et al., 2007).It is mainly used as fodder for animals and compost for nourishment of soil. Major part of these straw is not in use and is either discarded or brunt that causes air pollution and green house effect. Digestion of lignocellulosic material anaerobically is microbiological process that produce biogas consisting is of methane and carbon dioxide in the absence of oxygen. This gives a new way to consume the waste and to generate energy. This is cost effective resourceful and viable method for solving base problem (André et al., 2018)Studies has been shown that anaerobic digestion of these waste is sustainable and has great advantage over other methods because of its improved balance of energy. The process of biogas generation from crop residue and animal dropping has attracted the interest of scientists because of the numerous benefits realised from it. The main objective of the present study to investigate the potential of agriculture residual for bioenergy production and their application as a bio material for treatment of wastewater/production or other value added products.

2. Literature Review

Crop residues are lignocelluloses biomass with a yearly production of approximately 200 billion tons. They are the most abundant renewable source of energy production. Food wastes are also abundant waste that can be very useful for bio-energy production. Sravanthi Choragudi (2011) suggested that in India, as compare to the other renewable energy resources, biogas plants at domestic level is preferred source of renewable energy. Thus this shows that earliest technology for renewable energy has developed in India. for the formation of biogas, the substrate is converted in to slurry and undergo anaerobic digestion to produce biogas. Biogas is basically mixture of gases in which methane is in maximum amount. To convert the contents of crop residues in to methane, animal droppings are added. Stalin et al., (2007) modified three-stage methane fermentation system to digest animal droppings effectively. These three stages are hydrolysis, acetogenesis and methanogenesis. These can be carried out separately or in combination with each other. Anaerobic process in case of food waste digestion significantly improves the methanogenesis process as the fermentation shows significant role of pre-treatment,

thus improving the conversion efficiency of volatile fraction of biogas. The study examined the effects of microbes' growth, temperature and medium on biogas generation and hydraulic retention time. Tom band et al., (2011) studied technologies which recover biogas, that do so by harnessing anaerobic digestion or degradation pathways controlled by a suite of organisms. The ingredients of biogas are 50-70% of methane and 30-50% of carbon dioxide with traces of other gases.

To carry out Anaerobic digestion temperature plays very important role as depending upon temperature, the process may be mesophilic (about 35 ◦C), thermophilic (about 55 ◦C) or psychrophilic conditions (below 20 ◦C).

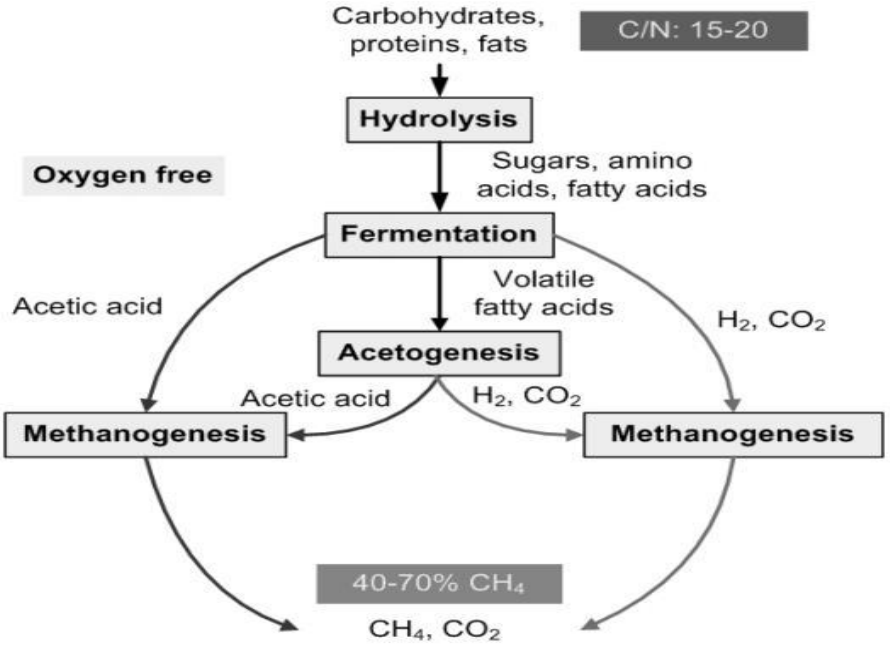

Figure 2: The biochemical stages of the anaerobic digestion process (Based on Gujer and Zehnder, 1983)

The kinetics production of biogas and the total capacity of a biogas plant depend on temperature. The hydraulic retention time i.e. the time period of experimental set up is 15–50 days, if it takes place in thermophilic conditions, this time period is 14-16 days and if takes place in psychrophilic conditions, this time period is 60-120 days (Marisa et al., 2019). Many experiments at full scale mesophilic process is most is easier to control, thus preferred (Nges et al., 2010)

Zhang et al., (2013) showed that anaerobic co-digestion of food waste and cattle manure increased the methane production by 41.1% with a methane yield of 388ml/g-VS,asa consequence of a C/N ratio of 15.8,coresponding to a FM/CM ratio of 2. Xiauyingliu et al., 2015 suggested that pre-treatment methods can be effective for enhancement of bio energy production. He used black liquor recycling for wheat straw pre-treatment and showed 18-20 % higher sugar yields & 33-41% higher methane yields than raw straw. The Pre-treatment with fresh KOH is more effective than pre-treatment with recycling of black liquor but still it is beneficial as it reduce chemical consumption by 25 % and use of water by 75 % as compare to a similar process without recycling. This shows that production of bio energy can be enhanced by developing chemically or biologically pre-treatment methods.

Co-digestion of two or more wastes has the following advantages:

• Produce relatively higher methane yield. For example, the energy production potential could be improved by 200% from the continuous co-digestion of food waste with manure than the digestion of manure alone (El-Mashad and Zhang, 2007-8). The microbial synergism effect makes a major contribution to the higher methane yield (Carucci et al., 2005).

• Provide balance nutrients. The C/N ratio of the major wastes such as manure is commonly as low as 8-15.The addition of the substrates with higher C/N such as food waste can provide more balanced nutrients (Montusiewicz et al., 2008).

• Increase the volume of available feedstocks. The volume of the wastes from one resource may be limited. For example, the amount of manure from one farm may be not sufficient for large-scale digester. The addition of other wastes can raise the capacity of the digester. .

• Improve the economics of AD facility. The addition of other wastes will make the digester more profitable especially considering the tipping fee of processing waste.

• Dilute toxic substance. Toxic substance in one feedstock may be diluted in co-digestion (Gomez et al., 2006). However, the industrial application of the co-digestion requires more knowledge on the selection of feed stocks and suitable mixing ratios.

3. Description of Broad Area

Crop Residue Or lignocellulosic Biomass is polymeric composite with cell walls made up of cellulose, hemicelluloses and lignin. Lignin provides strength and rigidity to the lignocellulosic material Hinder the depolymerisation of cellulose and hemicelluloses. As the chemical pretreatment is classified into physico-chemical, chemical, and thermo-chemical pretreatment, the physico-chemical pretreatment, referred to as combined chemical and mechanical pretreatment method is of many types like steam explosion, ammonia fibres explosion (AFEX) and carbon dioxide explosion. In steam explosion involves with the use of steam at a temperature and pressure between 160 and 260°C and 0.69– 4.83 MPa respectively, thereby hydrolyzing the hemicelluloses for the ease accessibility by microbes. Whereas, the AFEX process is performed with anhydrous ammonia at temperature and pressure that are between 60 to 100°C, and 1.72–2.07 MPa, respectively. It enables approximate complete reduction of the lignin and hemicelluloses content, and higher cellulose con- version. Similarly, the CO2 explosion requires the injection of CO2 at high pressure into the system and was shown to improve the enzymatic digestibility as well as the hydrolysis rate. Chemical pretreatments include mainly the addition of acids or alkalis and these treatments have been applied to animal manure. Chemical pretreatment could be carried out in combination with increased temperatures, in which it is referred to as a thermo- chemical pretreatment. Acid-based pretreatments use either dilute or strong acids to hydrolyze the hemicelluloses content and to solubilise and precipitate the lignin. Alkali pretreatment uses bases like sodium hydroxide (NaOH), lime (Ca(OH)2), and ammonia (NH3) to solubilise the lignin content .NaOH has been reported to cause the disruption of hydrogen bonding in the cellulose and hemicelluloses and also the breakage of ester link- ages between lignin and xylan, and the deprotonation of phenolic groups. In addition, Lopez Torres and Espinosa Llor´ens reported, that the NaOH yielded better solubilisation efficiency than the Ca(OH)2; therefore, it improves the anaerobic digestion performance. Similarly, NH3 has been found to cause swelling of cellulose and altering the structure of the crystal. But, its disadvantage is the higher cost of recovery. Whereas, the low cost and the safe handling of Ca (OH) 2 make it an economical chemical for pretreatment when compared to the NaOH and NH3.Presently, most of the alkali pretreatments use large amount of chemical solution and water to soak substrates, which require recycling of the chemicals, disposal of waste solution, and at times, high

temperature, hence, could lead to high facility investment, high treatment cost, and possible environmental pollution. Chemical pretreatments that use chemicals like acids, alkali, ammonia, peroxide, or organic solvents are mainly concentrated on the removal of lignin, which in turn leads to an improved degradation of cellulose by the microbes. This shows that lignocellulosic biomass can be converted into bioenergy products via the process of AD and this can be enhanced by chemical pretreatments.

4. Objective of research

- To investigate the potential of different bio-waste for bio-energy production.
- To study the influence of chemical treatments on lignin depolymerisation and anaerobic digestion process.
- To compare the efficacy of different chemical treatments for bioenergy production.
- To study the optimization of process parameters for optimum production of bioenergy.

5. Materials and Methodology

Parameters for substrate Characterization:

1. pH
2. Total Solids
3. Chemical oxygen Demand
4. Total Organic Carbon
5. Total Kjeldhal Nitrogen

Experimental design of the present study can be divided in following steps:

Selection and characterization of biomass feedstock

This step involves the study of biomass characteristics collected from different study sites. The analysis will be performed in terms of following parameters:

1. Total organic carbon
2. Total Nitrogen
3. Chemical Oxygen Demand

4. Lignin
5. Total carbohydrate
6. Moisture content
7. Volatile solid

Step 2: Fabrication of anaerobic digester and preparation of feedstock

is the preparatory stage for biogas production experiments and determines the process efficiency for biogas production. This step involves the feedstock preparation to be filled in digester. The whole step can be subdivided in to following sections:

(a) Sampling of agro food waste and its characterization.

(b) Designing of Biogas reactor.

(c) Preparation of slurry in 1:2 ratios.

(d) Setup of biogas reactor at different combination of agro food waste with different conditions.

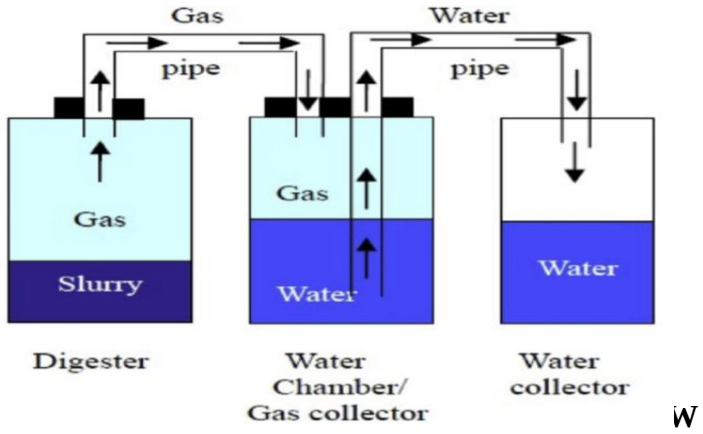

Figure 3: Schematic diagram of digester set up

Step 2: Downstream processing of production of bioenergy and value added products

Downstream processing can be stated as a monitoring and analytical step for biogas production. it not only involve monitoring of bioenergy production per day but also measures the amount of COD removed daily. The slurry remained after the completion of experiment was analyzed to observe nutrient and pollution load. Followings are the subsections of this step.

(a) Estimation of biogas production

(b) Biochemical analysis of slurry produced.

(c) Co-digestion and chemical biological treatments for getting the optimum conditions for maximum result of bioenergy production

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Regents, chemicals and glassware

Distilled water will be used for preparation of all regents so that we will get result with minimum error. All the apparatus and glassware will be washed followed by rinse with distilled water .All the chemical that will be used, are of analytical reagent grade.

Selection of substrates

Selection of proper substrate is very important to maintain the C/N ratio and to attain the proper HRT for bioenergy production. There are many choices available for biogas production from low to high quality, low to high cost, less available to abundantly available substrate i.e. untreated wastewater from dairy industry, poultry waste, algal biomass and cow dung from different places. The main focus of this research is to compare the bioenergy production rate of different co- waste materials at different temperatures.

So, the next step would be to investigate waste from different industries/ waste generating place for biogas production. Therefore, to promote the waste to energy concept for sustainable development, lignocellulosic biomass is good option due to abundant of carbohydrates in it.

Significance and novelty of purposed Work

Access to a safe ecosystem and undamaged natural resources is a public right because human health depends on the quality of the surrounding environment.lt is estimated that 38% of total global population uses solid biomass for home heating and cooking in poorly ventilated areas. Domestic and agricultural waste is a good source of renewable and economical resources of energy and provides biomaterials that can be used for wastewater treatment. This conversion of waste to useful products helps in recycling bio-mass in biosphere. Up gradation of bioenergy production technology from laboratory scale to industrial scale can be obtained by modifying the methods of bioenergy production, chemically or biologically. In the given study, chemically modified methods for bioenergy production will be investigated for commercial production and application of biomaterial for waste water treatment.

6. Expected outcomes

It is expected from the present study that the production of bioenergy will be enhanced by chemically modified methods of pre-treatment due to depolymerisation of cellulose, hemicelluloses and lignin.

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